

Using Simulation to Analyze the Effectiveness of  
Chitosan as a Green Kinetic Hydrate Inhibitor

By

Amro Abdelbadea Elsaghir Ahmed  
13449

Supervised by  
Siti Sarah Binti Salehudin

Dissertation submitted in partial fulfillment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Petroleum Engineering)

FYP II MAY 2014

Universiti Teknologi PETRONAS  
Bandar Seri Iskandar  
31750 Tronoh  
Perak Darul Ridzuan

# **CERTIFICATION OF APPROVAL**

## **Production Chitosan as a Methane Hydrate Green Inhibitor**

By

Amro Abdelbadea Elsaghir Ahmed Abdelfatah

13449

A project dissertation submitted to the

Petroleum Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

**BACHELOR OF ENGINEERING (Hons)**

**(PETROLEUM)**

Approved by,

---

Siti Sarah Binti Salahudin

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2006

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

---

AMRO ABDELBADEA ELSAGHIR AHMED

## ABSTRACT

Hydrate formation is a very important aspect in the field of gas flow assurance. Hydrates are ice-like formations that are composed of a cage of host molecules (water) entrapping guest molecules (gas). Some conditions must be met for the hydrates to be formed. These are low temperature, high pressure and the existence of water and gas molecules. The main objective of this study, after explaining about hydrate formation and studying means of inhibition is to produce a hydrate formation inhibitor with optimal concentration and degree of deacetylation, after simulating the function this inhibitor. After careful study and analysis, this inhibitor was chosen to be Chitosan, which is a green kinetic hydrate inhibitor.

The reason why hydrate inhibitors are needed in the field of gas production, processing and transportation is the major problems that are caused by the hydrate formation. Formation of hydrates inside the pipeline system can cause serious problems such as pipe blockage and corrosion. Pipeline blockage, or at least reduction of the internal diameter of the pipe as a result of hydrate accumulations, can also cause reduction in the production rates, which cost a significant amount of money. Furthermore, the common inhibitors nowadays are considered to be expensive and harmful to the environment. Therefore, this study aims to introduce a hydrate inhibitor that overcomes the limitations and disadvantages of the existing inhibitors.

The method of obtaining the inhibitor examined by this study, which is Chitosan, is from the outer skeleton of the crustaceans animals like shrimps. Then the Chitosan is prepared and tested in different deacetylation degrees and concentrations and simulated using Hydoff Software. The results are then analyzed to present the optimal concentration. But before that, the mixture of the gas that is to be used in the simulation is studied for its phase properties in order to know its normal phase properties so that those properties are to be compared with the gas mixture in contact with the inhibitor. These properties are determined using Hydoff Software.

## **ACKNOWLEDGEMENT**

First of all, I would like to thank Siti Sarah Salahudin, my main supervisor at Universiti Teknologi PETRONAS, for teaching me to have high standards and not to satisfy with less than the best, for being a model at how high dedication and self-discipline could reach, for giving me constant guidance and help; and most of all for constantly pointing out my mistakes and pushing me to do things in the right way.

I would like to thank also puan Mazuin Jasamai, from Petroleum Engineering Department at Universiti Teknologi PETRONAS, for helping me finish this report through teaching and guidance.

I would like to thank Mr. Mohd. Aslam, the Final Year Project Coordinator for the time and effort he puts into organizing the work and dividing the groups and presentations the kindness.

Last but not least I extend my appreciation to my family and friends and everyone who ever supported me or gave me a piece of advice to finish this work perfectly and on time.

# TABLE OF CONTENTS

## Contents

CERTIFICATION OF APPROVAL .....	i
CERTIFICATION OF ORIGINALITY .....	ii
ABSTRACT .....	iii
ACKNOWLEDGEMENT .....	iv
TABLE OF CONTENTS .....	v
LIST OF FIGURES .....	vii
CHAPTER 1 .....	1
INTRODUCTION .....	1
1.1 BACKGROUND .....	1
1.2 PROBLEM STATEMENT .....	1
1.3 OBJECTIVES .....	2
1.4 SCOPE OF STUDY .....	2
CHAPTER 2 .....	3
LITERATURE REVIEW .....	3
2.1 DEFINITION OF HYDRATES .....	3
2.2 HYDRATE TYPES .....	3
2.2.1 Type I Hydrate .....	3
2.2.2 Type II Hydrate .....	3
2.2.3 Type H Hydrate .....	4
2.3 HISTORY OF GAS HYDRATES .....	5
2.4 Hydrate Formation Conditions .....	6
2.5 HYDRATE FORMATION INHIBITION METHODS .....	8
2.5.1 Temperature Control .....	8
2.5.2 Pressure control .....	10
2.5.3 Dehydration .....	10
2.5.4 Injection of chemical inhibitors .....	11
2.6 NATURAL KINETIC HYDRATE INHIBITORS .....	14

CHAPTER 3 .....	16
METHODOLOGY .....	16
3.1 RESEARCH METHODOLOGY FLOW CHART.....	16
3.2 KEY MILESTONES .....	17
3.3 GANTT CHART .....	17
3.4 PROJECT ACTIVITIES.....	18
3.4.1 Research and Study:.....	18
3.4.2 Simulation:.....	18
3.4.3 Research Analysis:.....	18
3.5 SOFTWARE AND MATERIAL.....	18
CHAPTER 4 .....	20
RESULTS AND DISCUSSION.....	20
4.1 MATERIAL.....	20
4.2 SOFTWARE.....	21
4.3 SIMULATION PROCEDURE.....	22
4.3.1 Methane (99.95%) with distilled water.....	22
4.3.2 Determining the best Degree of Deacetylation of Chitosan. ....	27
4.3.3 Determining the optimum Chitosan concentration of 85% DD.....	29
CHAPTER 5 .....	32
CONCLUSION AND RECOMMENDATION.....	32
REFERENCES .....	33

# LIST OF FIGURES

Figure 1: Type I and Type II Hydrate structures [1] .....	4
Figure 2: Major Methane Hydrate Fields [2].....	6
Figure 3: Pressure-Temperature curves for predicting hydrate formation [4].....	7
Figure 4: Triangle representing hydrate formation conditions. ....	8
Figure 5: Hydrate Equilibrium Curves for Gas Analysis Comparison [6] .....	9
Figure 6: Line heater anatomy [5]. ....	9
Figure 7: Glycol dehydration unit. [6].....	11
Figure 8: Effect of Thermodynamic Hydrate Inhibitors (THI) on dissociation curves [8]. ....	12
Figure 9: Chitosan Chemical Structure (Xu et al., 2010). ....	15
Figure 10: Research Flow Chart.....	16
Figure 11: Project Key Milestones .....	17
Figure 12: Project Gantt Chart .....	17
Figure 13: Schematic diagram of Hydreval.....	22
Figure 14: Unit system to be used by CSMGem Software.....	23
Figure 15: Input method .....	23
Figure 16: Number of gas components. ....	24
Figure 17: Identifying the components in the gas mixture.....	24
Figure 18: Input mole fraction of each component. ....	25
Figure 19: Equilibrium Pressure.....	26
Figure 20: Specified T and P Flash .....	26
Figure 21: Induction time for the restored gas composition.....	27
Figure 22: Induction time vs DD (0.5wt%).....	29
Figure 23: Induction time (min) vs wt% (85% DD).....	30



## LIST OF TABLES

Table 1: Chemical formulae for glycols used in dehydration process [7].	10
Table 2: Gas composition to be used.	21
Table 3: Simulation of different DD of Chitosan (0.5 wt%).	28
Table 4: Simulation of different concentrations of Chitosan with a DD of 85%.	30

# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND

Hydrate formation inhibition is a very important aspect of the gas flow assurance in the pipeline system. Hydrates are formed under certain conditions where water molecules and gas molecules are present, at low temperatures and high pressures. Hydrates can be formed in the pipelines after production as well as naturally, mostly in the intermediate offshore environment where the conditions are met. The structure of the hydrate is very similar to that of ice. However, it is not purely made up from water molecules, but also gas molecules are found compressed inside a cage made up from water molecules. Previously, hydrate formation was common in Alaska, the Gulf of Mexico and Japan. But now, it is relatively new to be found in Malaysia.

### 1.2 PROBLEM STATEMENT

**1.2.1 Blockage of the pipeline.** Formation of hydrates in the pipeline can block the gas flow inside the pipeline at the points which are not subject to full flow such as orifice plates and valves; and it is very expensive to fix the problem in the pipeline after being plugged.

**1.2.2 Reducing the production.** Hydrate formation can also retard the gas flow inside the pipeline causing the production to be reduced.

**1.2.3 Corrosion problems.** When water in the liquid phase coexists with acidic gases, an acidic solution is resulted and corrosion becomes a high possibility especially to carbon-steel pipes, which are widely used in the hydrocarbon processing facilities.

**1.2.4 Inhibitors** used so far are not economic enough and are not eco-friendly.

### **1.3 OBJECTIVES**

1.3.1 To determine the properties of the gas mixture to be used alone without the inhibitor.

1.3.2 To study the effectiveness of Chitosan as a Green Kinetic Hydrate Inhibitor (KHI) using Hydoff Software.

1.3.3 To compare the effectiveness of Chitosan at with different deacetylation degrees and concentration.

1.3.4 To determine the optimal deacetylation degree and concentration of Chitosan to be used as Methane Hydrate Inhibitor.

### **1.4 SCOPE OF STUDY**

The focus of this research is on the study of hydrate formation conditions and the various ways to inhibit their formation. However, the research is more focused on Chitosan as a Green Kinetic Hydrate inhibitor (KHI). During this research, simulation will be conducted using Hydoff software to study the effectiveness of different deacetylation degrees and concentrations of Chitosan and their capacity to inhibit (or delay) the formation of methane hydrates. This simulation is to be conducted at a temperature of 274.3 K and a pressure of 4,500 kPa.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 DEFINITION OF HYDRATES

Formation of hydrates is a major flow assurance concern in the gas transportation systems. Hydrates are ice-like crystals that are formed in certain conditions and with certain composition. Hydrates are formed as a result of the hydrogen bond between the water molecules, which are also called “host”; and the hydrocarbon molecules, which are called “guests”; or sometimes “formers”. Because of this hydrogen bond, the resultant crystalline is very stable. Steam (host) molecules form cages that entrap the hydrocarbon (guest) molecules. [1]

#### 2.2 HYDRATE TYPES

Gas hydrates are classified based on the arrangement of water (host) molecules in the crystal [1]. See Figure 1.

**2.2.1 Type I Hydrate:** It has the simplest hydrate structure. It has 46 molecules of water (host) molecules. The guest molecules can be methane, ethane, carbon dioxide or hydrogen sulfide. It includes two shapes:

- i. Dodecahedron: which has 12 sides of polyhedrons each side is a pentagon.
- ii. Tetrakaidecahedron: which has 14 sides of polyhedron, 12 of which are pentagons and the other 2 are hexagons.

**2.2.2 Type II Hydrate:** It has 136 water (host) molecules. The guest molecules can be propane, iso-butane or nitrogen. It also includes two shapes:

- i. Dodecahedron: like Type I, has 12 sides of polyhedrons each side is a pentagon.

ii. Tetrakaidecahedron: which has 16 sides of polyhedron, 12 of which are pentagons and the other 4 are hexagons.

**2.2.3 Type H Hydrate:** It is less common than Type I and II. It has 36 molecules of water (host). Two types of guest molecules exist in one unit, unlike the previous types; which are a small molecule; such as methane and larger host molecules such as cyclohexane. The larger molecules are not components of natural gas, that's why Type H hydrate is very uncommon. Therefore, most of the experiments are not done on it. It includes 3 shapes:

- i. Dodecahedron: like Type I and II, has 12 sides of polyhedrons each side is a pentagon.
- ii. Irregular dodecahedron: which has 3 square sides, 6 pentagon and 3 hexagons.
- iii. Irregular Icosahedron: which has 20 sides of polyhedrons, 12 of which are pentagons and 8 are hexagons.

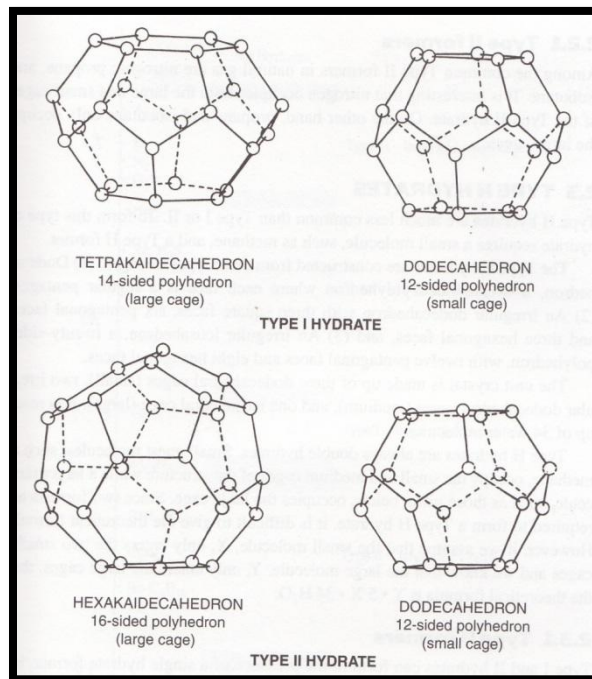


Figure 1: Type I and Type II Hydrate structures [1]

## 2.3 HISTORY OF GAS HYDRATES

The first one to study gas hydrates might have been the English chemist Humphery Davy in the early 1800s. However, Davy's assistant Michael Faraday was the one who got the credit officially after filing a report in 1823. The report describe an ice-like substance that held the guest molecules inside of it. Humphery called that substance as “chlorince clathrate hydrate”. [2]

Hydrates were only subject to laboratory experiments until the 1930s when the natural-gas miners complained from the blockage of the pipelines due to some solid that were formed at low temperature parts. Scientists and chemists examined that solid, they found that it was not purely made of ice, but there was compressed methane inside it. Since then, the gas producing companies have been using the gas hydrate inhibitors. [2]

However, in the 1960s, the first naturally occurring methane hydrate was found in Messoyakha field in Western Siberia. After a few years, methane hydrate was also found in sediments buried deep in the slope of Alaska. Researches, chemists and geologists took the opportunity to explore the environment that helped hydrates to form naturally. Years later, the United States Geological Survey made researches on hydrates and reached a conclusion that offshore sediments are good environments for the formation of the hydrates. That research was made between 1982 and 1992. In the mid-1990s, after spreading these results, many countries, especially India and Japan, started to search for hydrate deposits. Figure 2 shows the major methane hydrate fields that were discovered back then, most of which are offshore fields as shown.

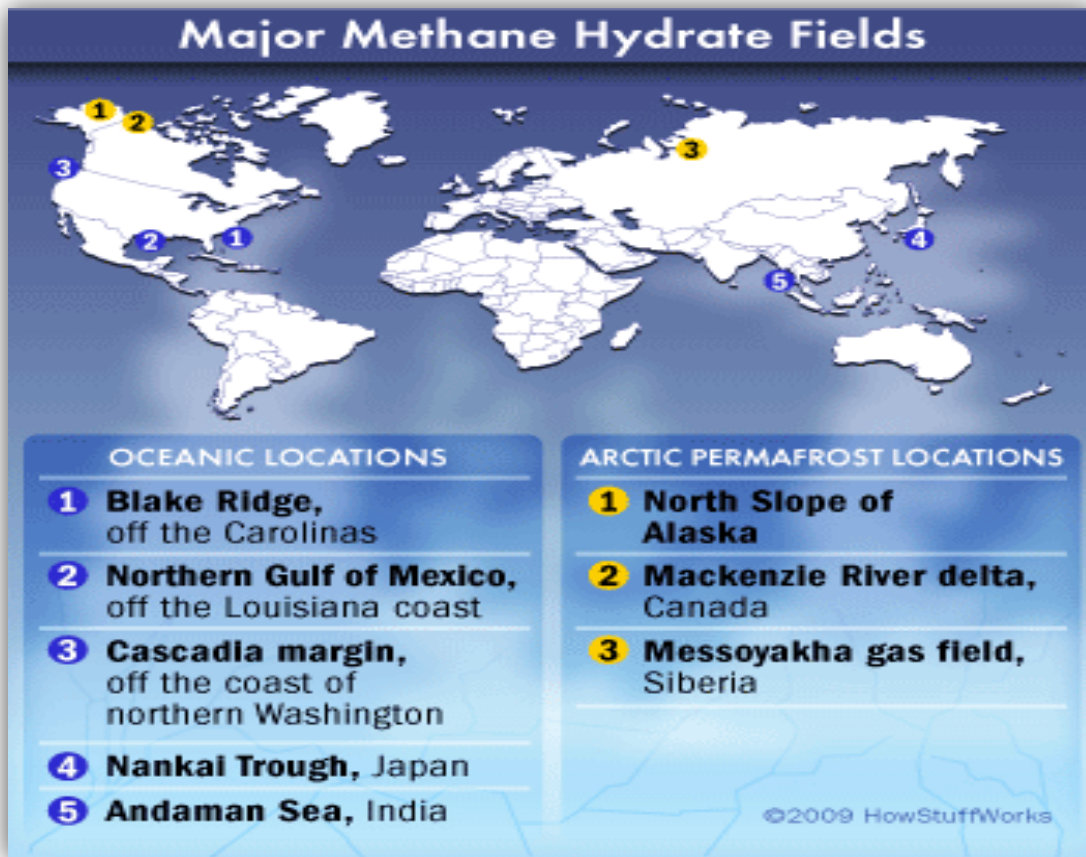


Figure 2: Major Methane Hydrate Fields [2].

## 2.4 Hydrate Formation Conditions

For the hydrate to be formed, three conditions must be met, which are represented by a triangle, see Figure 4. That's why researchers on the hydrate inhibitors are always doing their best in order to find a way to break one of the sides of the triangle. [3][4] These conditions as:

**2.4.1 The presence of free water molecules (host) and the guest (former) molecules.** The source of the free water molecules is from either the reservoir or condensing the hydrocarbon fluid after cooling and condensing.

**2.4.2 Low temperatures.** Hydrates do not need temperatures lower than 32°F (0°C) in order to be formed. It can be even formed at temperatures as high as 70°F at high pressures.

**2.4.3 High pressures.** The pressure needed for the hydrate to be formed depends on the temperature, the type (gravity) of the gas (guest). Figure 3 shows a graph that can help determine one parameter knowing the other two. The parameters are: pressure (psia), temperature (°F) and the gas gravity.

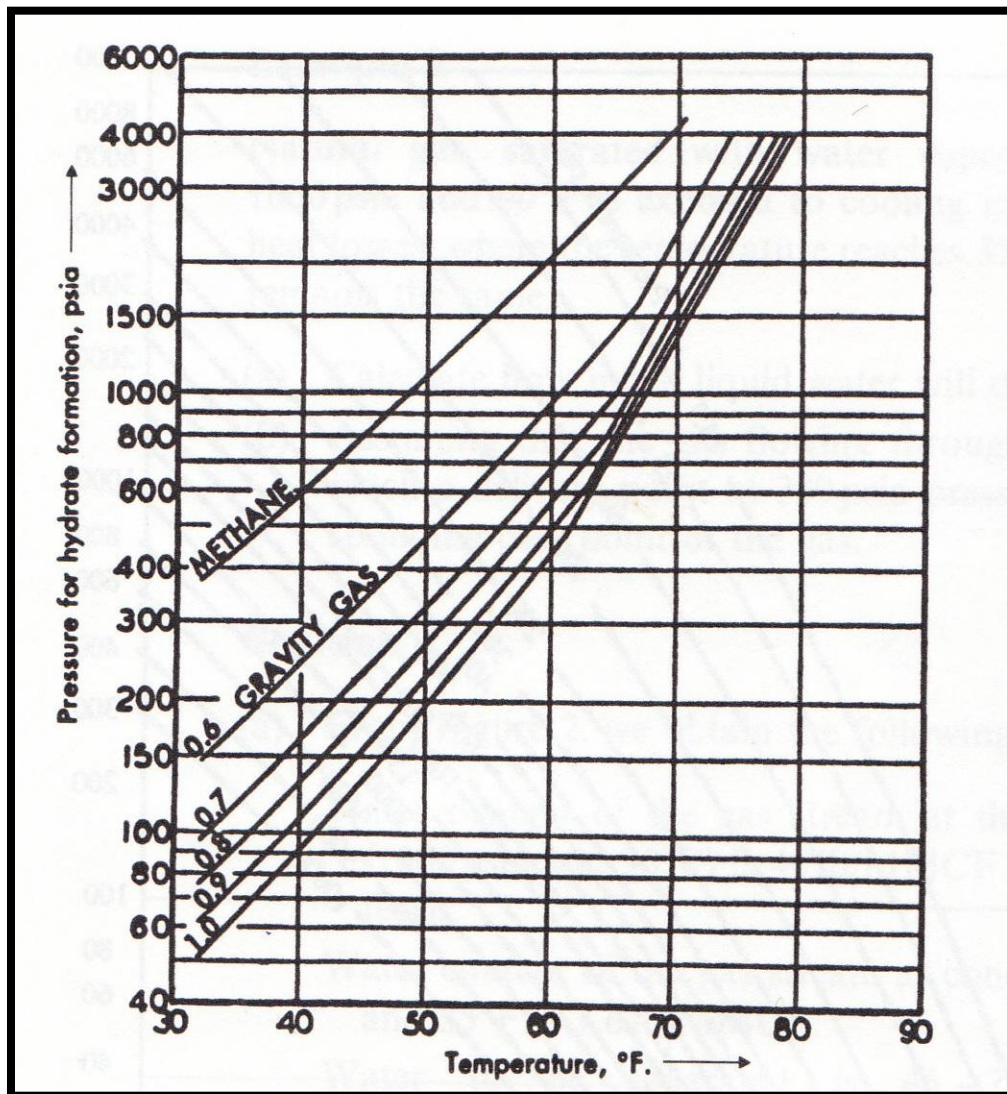


Figure 3: Pressure-Temperature curves for predicting hydrate formation [4].



## 2.5 HYDRATE FORMATION INHIBITION METHODS

Recalling the conditions of hydrate formation, they can be represented by the triangle in Figure 4, where each corner of the triangle represents a condition. Logically, in order to prevent the formation of hydrates, at least one corner of the triangle must be broken. The choice of the most suitable method depends on the system that needs to be controlled. That's why, a full understanding of the system is necessary to choose the right method [5]. Considering the triangle mentioned earlier, hydrate formation can be inhibited by the following methods:

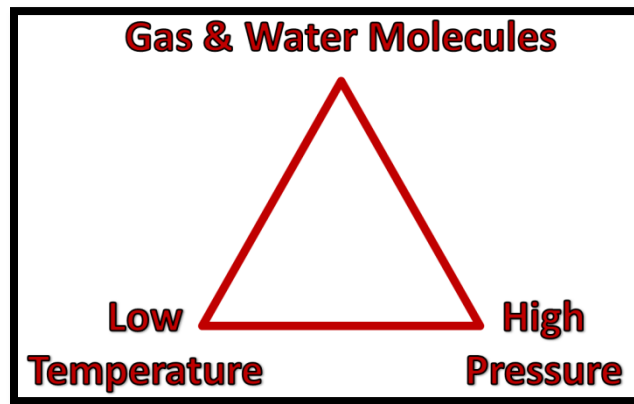


Figure 4: Triangle representing hydrate formation conditions.

**2.5.1 Temperature Control.** Increasing the temperature of the system so that the temperature at which the hydrate forms is overcome. Hydrate formation temperature is determined from the hydrate equilibrium curve of the system, see Figure 5. Line heaters are used for that purpose. Line heaters are installed at the points in the well sites and the pipeline transportation systems at which the pressure drops significantly causing the temperature to be reduced and the hydrates to be formed. [6]

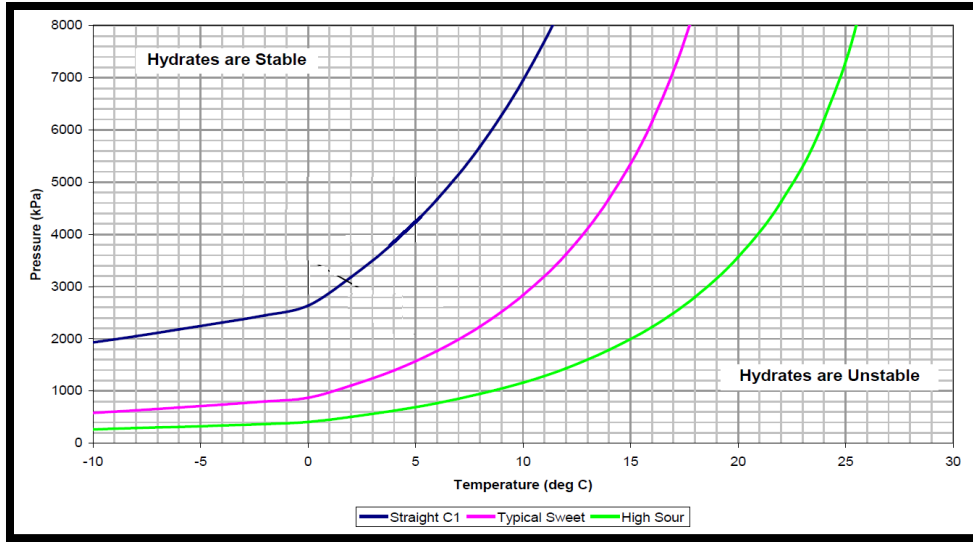


Figure 5: Hydrate Equilibrium Curves for Gas Analysis Comparison [6]

Line heaters, shown in Figure 6, have some disadvantages such as consuming a lot of fuel gas, the high probability of blockage because of scale build up and increasing the chances of corrosion occurrence. To minimize the loss of heat to the surroundings, thermal insulations can be added. However, it is very expensive. [5]

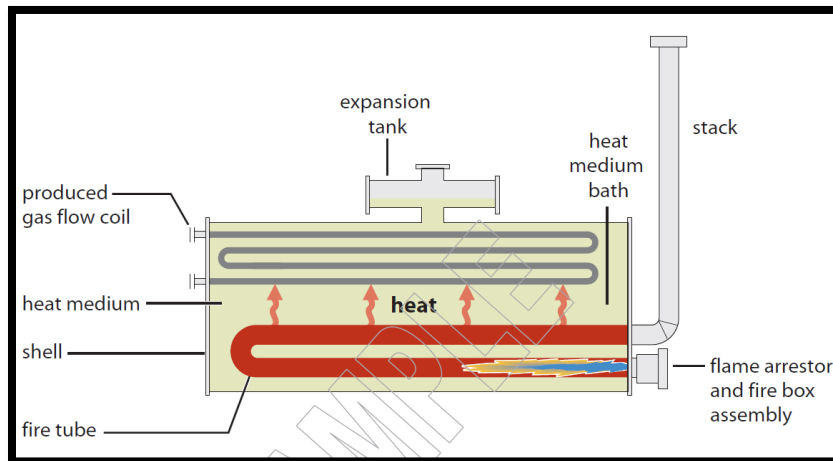


Figure 6: Line heater anatomy [5].

**2.5.2 Pressure control.** The pressure of the system can also be reduced to pressures below the hydrate formation pressures to values based on the hydrate equilibrium curves like the case in Figure 5.

The drawback of this method is that lowering the pressure will cause a reduction in the flow rates, thus the production will reduce and more time will be consumed sparing more expenses. That's why this method is not widely common. [5]

**2.5.3 Dehydration.** The second corner (option) of the triangle that needs to be broken in order to prevent hydrate formation is the condition of water existence. Of course, the gas molecules cannot be touched or reduced because gas is the desired product. Therefore, the molecules that can be reduced are the host molecules (water) which is done by the dehydration process [7]. Dehydration covers two processes which are absorption and adsorption. In this study, the absorption process is going to be described briefly since it is the most commonly used process of dehydration.

Absorption is the process in which the gas passes in contact with a liquid which, in turn, absorbs only water vapor. The absorbents that are commonly used to absorb water vapor are glycols; such as ethylene glycols (EG), di-ethylene glycols (DEG), tri-ethylene glycols (TEG), tetra-ethylene glycol (TREG) and even propylene glycol. The chemical structure of each type is listed in Table 1.

Table 1: Chemical formulae for glycols used in dehydration process [7].

Name	Structure	Formula
Ethylene glycol (EG)	HO-(CH <sub>2</sub> ) <sub>2</sub> -OH	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>
Di-ethylene glycol (DEG)	HO-((CH <sub>2</sub> ) <sub>2</sub> -O)- (CH <sub>2</sub> ) <sub>2</sub> -OH	C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>
Tri-ethylene glycol (TEG)	HO-((CH <sub>2</sub> ) <sub>2</sub> -O) <sub>2</sub> - (CH <sub>2</sub> ) <sub>2</sub> -OH	C <sub>6</sub> H <sub>14</sub> O <sub>4</sub>
Tetra-ethylene glycol (TREG)	HO-((CH <sub>2</sub> ) <sub>2</sub> -O) <sub>3</sub> - (CH <sub>2</sub> ) <sub>2</sub> -OH	C <sub>8</sub> H <sub>18</sub> O <sub>5</sub>
Propylene glycol	HO-(CH <sub>2</sub> ) <sub>3</sub> -OH	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>

Of course, the choice of the proper glycol type depends on the situation. The most commonly used absorbent is tri-ethylene glycol (TEG). However, for cold environment operations, di-ethyl glycol (DEG) is preferred. As for ethylene glycol (EG), it is used when brine is existed ionized in the water vapor. The reason is that ethylene glycol (EG) has the dissolve sodium chloride up to 20%wt. Tetra-ethylene glycol (TREG) is rarely used because of its high cost. [6] Figure 7 shows a glycol dehydration unit.

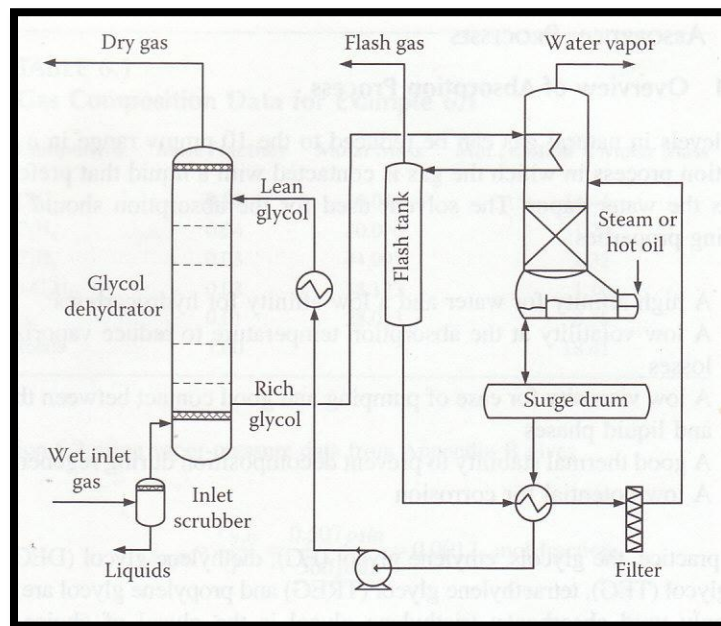


Figure 7: Glycol dehydration unit. [6]

**2.5.4 Injection of chemical inhibitors.** There are different types of chemicals that are injected in the system to prevent hydrate formation. These chemicals can be classified into four (4) main categories:

2.5.4.1 Thermodynamic Hydrate Inhibitors (THI). As it is obvious from its name, thermodynamic hydrate inhibitors are chemical compounds that are injected into the system so that it modifies the thermodynamic stability of the hydrates. This is done, as shown in Figure 8, by lowering the hydrate

formation (operating) temperature ( $T_{op}$ ) to a value less than the dissociation temperature ( $T_{diss}$ ); or by increasing the hydrate formation (operating) pressure ( $P_{op}$ ) to a value more than the dissociation pressure ( $P_{diss}$ ). An example of these inhibitors is methanol and mono ethylene glycols (MEG). [8] A helpful analogy to understand the function of these inhibitors is the addition of anti-freeze material to water lowering its freezing point. [8]

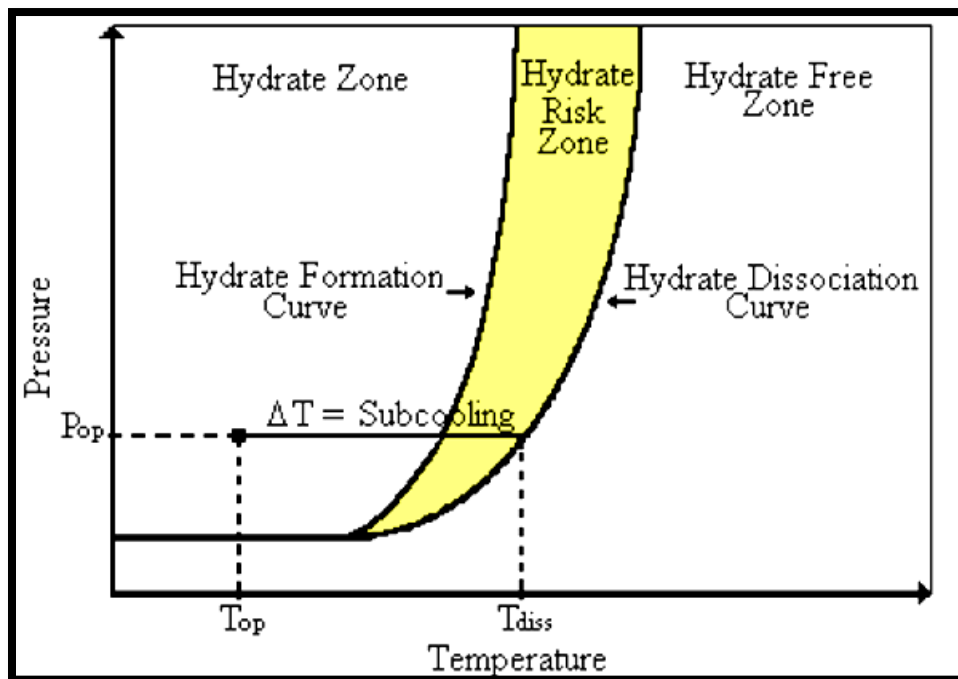


Figure 8: Effect of Thermodynamic Hydrate Inhibitors (THI) on dissociation curves [8].

A lot of advantages for this type of inhibitor (THI) made it the most common worldwide. [8] Some of these advantages are:

- ✓ Reduction of hydrate formation temperature.
- ✓ Number of softwares are available for measurement.
- ✓ Compatibility of functioning in any hydrocarbon system.

However, thermodynamic hydrate inhibitors (THI) have some drawbacks and limitations, which motivated researches to develop other chemicals; such as:

- ❖ Large space required for storage.
- ❖ High pumping requirements.
- ❖ Corrosion problems.
- ❖ Environmental concerns.

2.5.4.2 Low Dosage Hydrate Inhibitors (LDHI). This is a newly-developed type of inhibitors. These include two types of inhibitors, that are going to be discussed in the next two sections, which are Kinetic Hydrate Inhibitors (KHI) and Anti-agglomerants (AA) [9].

2.5.4.3 Kinetic Hydrate Inhibitors (KHI). Their function is to delay and retard the formation and crystal accumulation of hydrates for a period of time that can be estimated. The mechanism of these inhibitors is that they bind with the hydrates in the early stages of their formation and prevent them from accumulation and growing to reach the critical size. The period of time along which the hydrate formation is inhibited varies from hours to days, giving the opportunity for the gas to leave the pipeline system before forming hydration. However, these inhibitors are unable to solve the already-formed hydrates. [9]

Kinetic Hydrate Inhibitors can be effective at concentrations as low as 1%wt. The effect of kinetic hydrate inhibitors do not depend on the amount of water. So as the reservoir depletes, the water cut gets higher. In such cases, kinetic hydrate inhibitors (KHI) have advantages over the thermodynamic inhibitors (THI). Some examples of (KHI) are: polyvinylpyrrolidone (PVP) which have been proven to be a good kinetic hydrate inhibitor based on experimental data of more than 750 different chemical compounds. [9]

2.5.4.4 Anti-Agglomerants (AA). Their function is to inhibit the agglomeration of hydrates so that they can be carried away in the form transportable mobile slurry. In other words, they allow the formation of hydrates, but they inhibit their agglomeration in order not to give hydrates the chance to grow enough to block or plug the pipeline system. Same as kinetic hydrate inhibitors (KHI), anti-agglomerants (AA) are also added in low concentrations. [9]

## **2.6 NATURAL KINETIC HYDRATE INHIBITORS.**

The definition and the mechanism of the kinetic hydrate inhibitors (KHI) were explained in the last section. However, kinetic hydrate inhibitors (KHI) are synthetic polymers which make them relatively expensive to prepare. Recently, there is a trend to develop and produce what is called “Green Hydrate Inhibitors”; such as Chitason, Starch, Anti-Freeze Proteins (APF) and Anti-Freeze Glyco-Proteins (AFGP). [10]

The focus of this study is on Chitason as a Natural (Green) Kinetic Hydrate Inhibitor. The reasons of this choice are illustrated in the discussion section. Chitason is defined as: “Chitosan is a linear polysaccharide composed of randomly distributed  $\beta$ -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit)”, see Figure 9. [10][11] Commercially, Chitason is a product of chitin deacetylation. Chitin is a structural component in the crustaceans’ outer skeletons. Examples of these crustaceans are crabs and shrimps shells.

Chitason production from the industry of waste food is economic and efficient. To produce 1 KG of acetylated Chitosan from the shells of shrimps, it is required to have 6.3 KG of hydrochloric acid (HCl) and 1.8 KG of Sodium Hydroxide (NaOH) as well as process and cooling water; and nitrogen. [10]

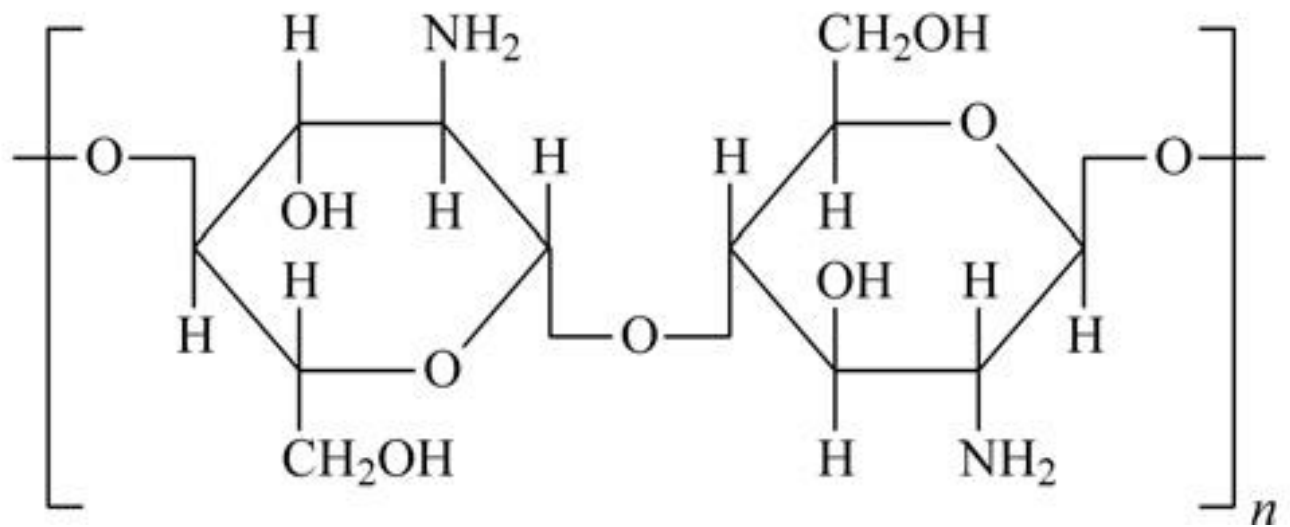


Figure 9: Chitosan Chemical Structure (Xu et al., 2010).

The effectiveness of different hydrate inhibitors is characterized by some parameters. One of the most important parameter is induction time. Induction time is defined as the time taken for the hydrate nuclei to reach the critical size to start and initiate the hydrate growing. [12]



## CHAPTER 3

### METHODOLOGY

#### 3.1 RESEARCH METHODOLOGY FLOW CHART

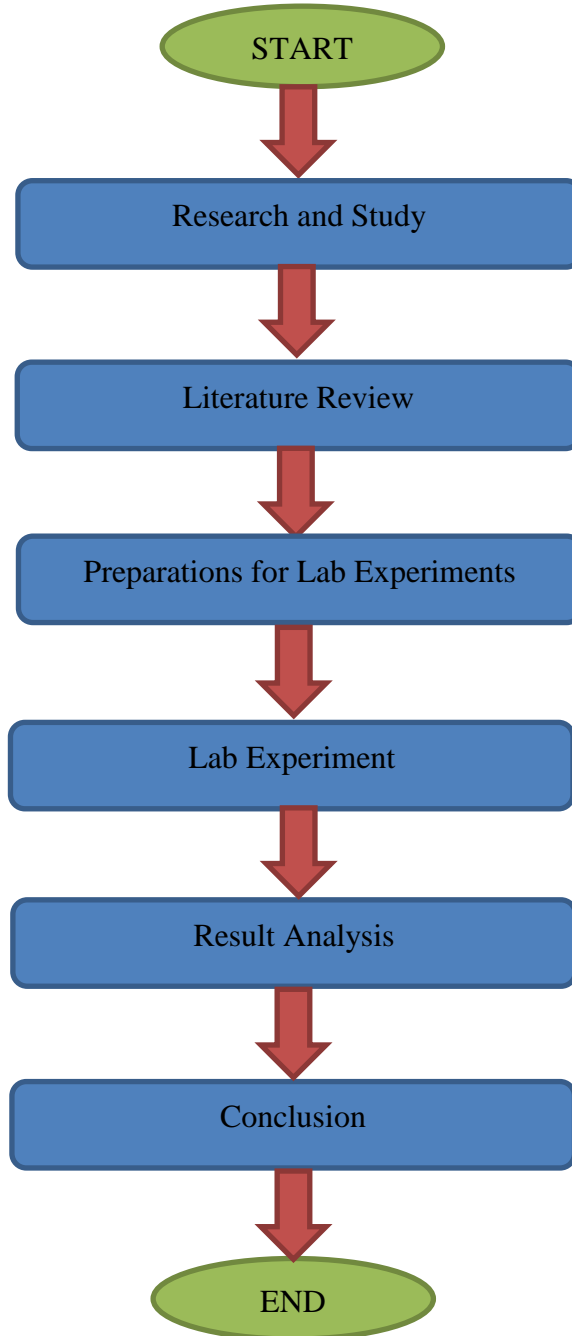


Figure 10: Research Flow Chart

### 3.2 KEY MILESTONES

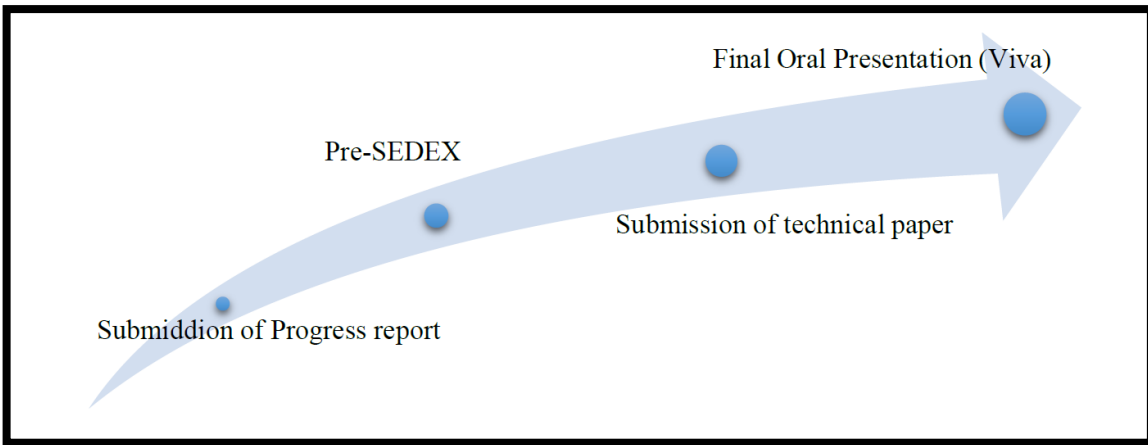


Figure 11: Project Key Milestones

### 3.3 GANTT CHART

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Process Simulation	Done	Done	Done	Done	Done	Done									
Writing the Progress report					Done	Done									
Progress report first draft submission							Done								
submission of Progress report								Done							
Lab experiments								Done	Done	Done	Done	Done			
Pre-SEDEX										Done	Done				
Writing the Final Report									Done	Done	Done				
Final Report First draft Submission										Done					
Submission of Final Report											Done				
Dissertation Submission (soft copy)												Done			
Technical Paper Submission													Done		
Viva													Done		
Dissertation submission (Hard Copy)															Done

Done	Done
To do	To do

Figure 12: Project Gantt Chart

### **3.4 PROJECT ACTIVITIES**

#### **3.4.1 Research and Study:**

- ❖ Research on hydrate formation.
- ❖ Research on hydrate inhibitors.
- ❖ Analyze and determine a target inhibitor to be produced.

#### **3.4.2 Simulation:**

- ❖ Determine the gas mixture to be used, based on the composition available in UTP labs.
- ❖ Perform simulations on that gas mixture and determine its equilibrium and hydrate conditions.
- ❖ Determine the optimal Deacetylation Degree of Chitosan.
- ❖ Range of DD: 60% to 90%.
- ❖ Simulation Temperature: 274.3 K.
- ❖ Simulation Pressure: 4,500 kPa.
- ❖ Manipulation of Chitosan concentrations to determine the optimum.

#### **3.4.3 Research Analysis:**

- ❖ Compare the effectiveness of different DDs of Chitosan with a constant concentration.
- ❖ Choose the optimal DD which gives the highest induction time.
- ❖ Compare the effectiveness of different concentrations of Chitosan with a constant DD.
- ❖ Choose the optimal DD and concentration.

### **3.5 SOFTWARE AND MATERIAL**

3.5.1 Hydoff Software for the prediction of hydrate phase equilibrium. Hydoff is developed by the research center at the department of Chemical and Petroleum-Refining Engineering Department at the Colorado school of mines. This program simulates the phase equilibrium conditions of hydrates given the composition of the gas mixtures. It can also calculate the induction time for the hydrates to be formed. [3]

3.5.2 Chitosan is used as a green Kinetic Hydrate Inhibitor in the simulation process. The samples can be ordered from Zhejiang Golden-Shell Biochemical Co. in China. Different degrees of deacetylation are simulated, which are 60%, 70%, 80% and 90%. First the best degree of acetylation is determined by the simulation. Then the best concentration of the best degree of deacetylation of Chitosan is estimated.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 MATERIAL

As a result of this intensive research, it was found that Methanol and Mono-Ethylene Glycols (MEG) are examples of Thermodynamic Hydrate Inhibitors and they are the most commonly used worldwide because of their many advantages. On the other hand, Thermodynamic Hydrate Inhibitors also have limitations and disadvantages. For that reason, the trend of the researches in the field of hydrate inhibitors has increased towards Low-Dose Hydrate Inhibitors, which are basically composed of two different classes of inhibitors: Kinetic Hydrate Inhibitors (KHI) and Anti-Agglomerants (AA).

As the development goes on, new kinetic inhibitors are being introduced or discovered. Recently, the researchers have focused on Natural Kinetic Hydrate Inhibitors, which are type of KHI, but naturally occurring. These new inhibitors have become the focus because they are nature-friendly, easy-to-prepare and, therefore, commercial compared to synthetic KHI.

Anti-freeze proteins, anti-freeze glycol-proteins, starch and Chitosan are examples of green (natural) KHI. In this research, the inhibitor chosen to study is Chitosan because, considering the climate in Malaysia, it seems to be the most preferable choice. This is because they are brought from the exoskeleton crustaceans; such as shrimps and crabs. Given the geographic location of Malaysia which is rich in the marine environment, these options seem to be highly available in comparison with antifreeze proteins that are extracted from the fish body that lives in cold and freezing environments.

For this simulation, a gas mixture of a composition as shown in Table 2 will be used for simulating and analyzing the hydrate formation conditions with and without inhibitor. The justification of using this composition is that, this is the exact composition used at

the labs of Universiti Teknologi PETRONAS. Therefore, the results of the simulation can be confirmed later by further practical experiments.

Table 2: Gas composition to be used.

Component	Mole %
CH <sub>4</sub>	99.95
CO <sub>2</sub>	00.05

## 4.2 SOFTWARE

The software to be used is Hydoff, which is developed by the research center at the department of Chemical and Petroleum-Refining Engineering Department at the Colorado school of mines. This program simulates the phase equilibrium conditions of hydrates given the composition of the gas mixtures. It can also calculate the induction time for the hydrates to be formed.

The simulation assumptions are based on the parameters that are used to operate the Hydreval, which is an equipment used to measure the thermal stability of hydrates and to determine the vapor-liquid equilibrium conditions of hydrates. [13] Hydreval is based on a PVT equilibrium cell that is driven by motor. The maximum capacity of the cell is 80 cm<sup>3</sup>. The device operates on a temperature range of -20 °C to 150°C and a maximum pressure of 20 MPa (2,900 psi). PVT properties are controlled using the Hydreval software and are recorded every 2 seconds. There is also a camera connected to a monitor to record the interface between the liquid and the gas phases. Liquid and gas are injected into the sapphire using an external pump. [14] Figure 13 shows the Hydreval.

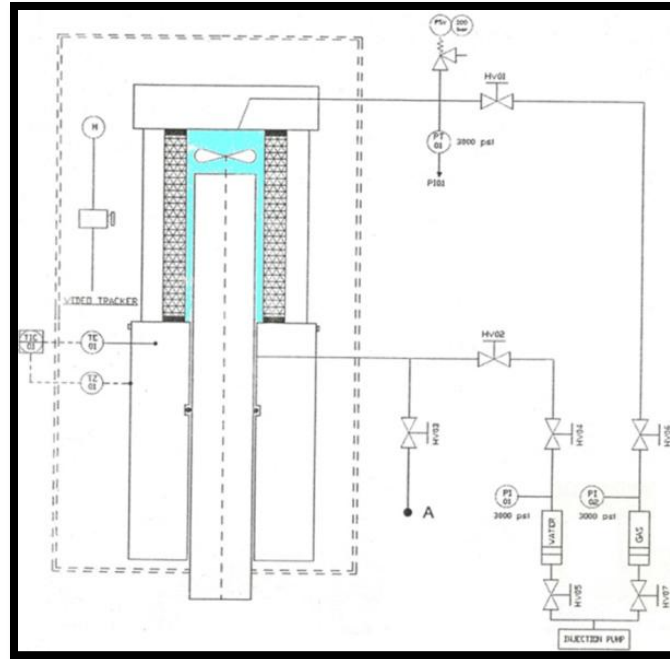


Figure 13: Schematic diagram of Hydrevall.

The conditions, on which this simulation is based, are:

- Constant temperature: 274.3 K
- Constant pressure: 4,500 kPa
- Gas Volume: 55 cc
- Water/Solution volume: 25 cc

## 4.3 SIMULATION PROCEDURE

### 4.3.1 Methane (99.95%) with distilled water.

It is necessary to start off by studying the properties and hydrate formation conditions for this gas mixture. As shown in the figures from Figure 14 to Figure 21, Hydoff software was used to simulate the conditions and the phase equilibrium. The method of using that software is illustrated here on.

First, the software asks to input the desired system of unit. For this case, Kelvin was chosen to express temperature and kPa was chosen to express pressure.

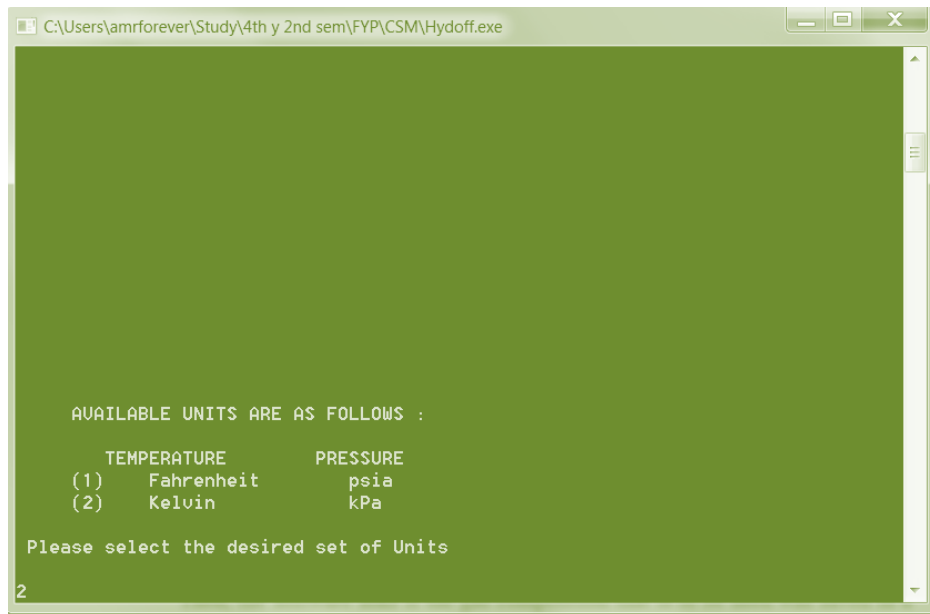


Figure 14: Unit system to be used by CSMGem Software.

Then, the software asks if the gas composition that is to be used was saved in an external data file or if the user wants to input it manually.



Figure 15: Input method



Afterwards, the software asks the user to input the number of the components existed in the gas mixtures; which are, in this case, 2.



Figure 16: Number of gas components.

After that, the user is asked to specify the components that are present in the mixture by choosing the corresponding number. As previously mentioned, the components are Methane and Carbon Dioxide.

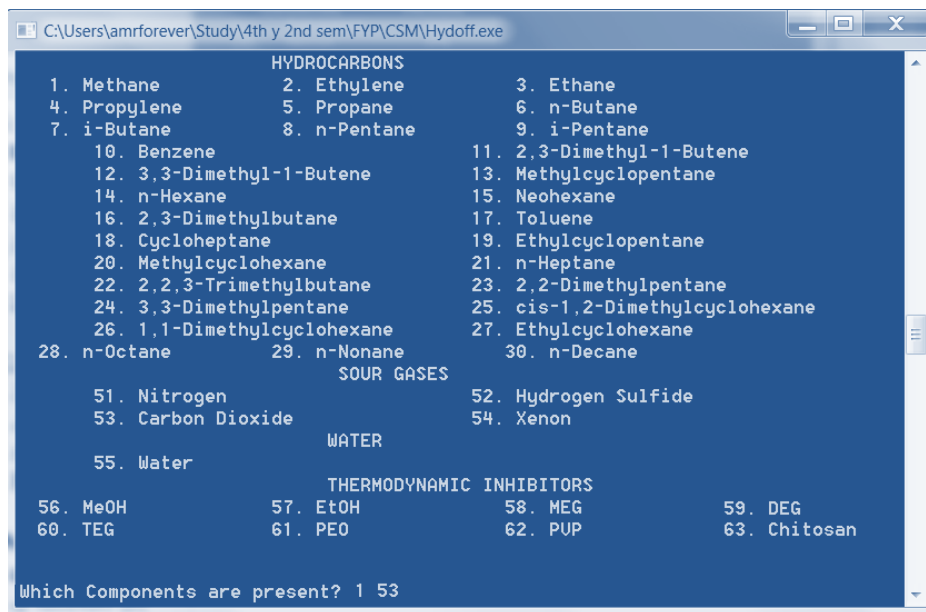


Figure 17: Identifying the components in the gas mixture.

The next step, the user is to input the mole fraction of each component in the mixture as stated in Table 2.

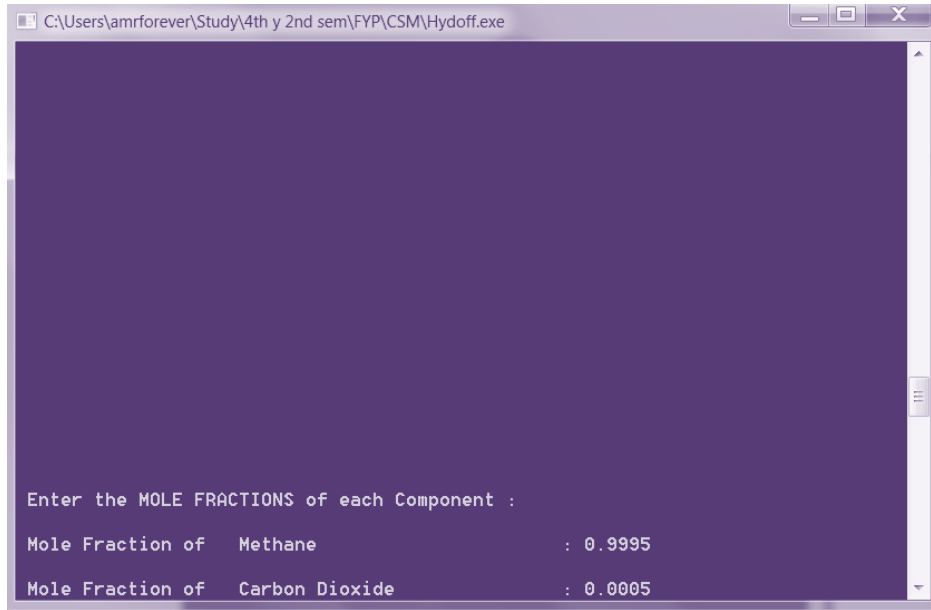


Figure 18: Input mole fraction of each component.

Now the user is asked to choose the desired function. Based on the objectives of this research and simulation, the option “Pressure prediction at a given temperature is chosen.

Afterwards, the software asks about the temperature at which the equilibrium conditions are studied. As mentioned earlier, the conditions, under which the behavior is studied, are 243.4 K and 4,500 kPa. Therefore, the value of temperature to be keyed in is 274.3 K.

Figure 19 shows the result of this simulation which shows that the equilibrium pressure at 274.3 K is 2934.604 kPa. And since the real conditions of experiment using the Hydreval, which are being simulated, are placed under 4,500 kPa which is more than the equilibrium pressure. Therefore, placing this gas mixture under a temperature of 274.3 K and a pressure of 4,500 kPa definitely falls in the hydrate formation region in its phase diagram.

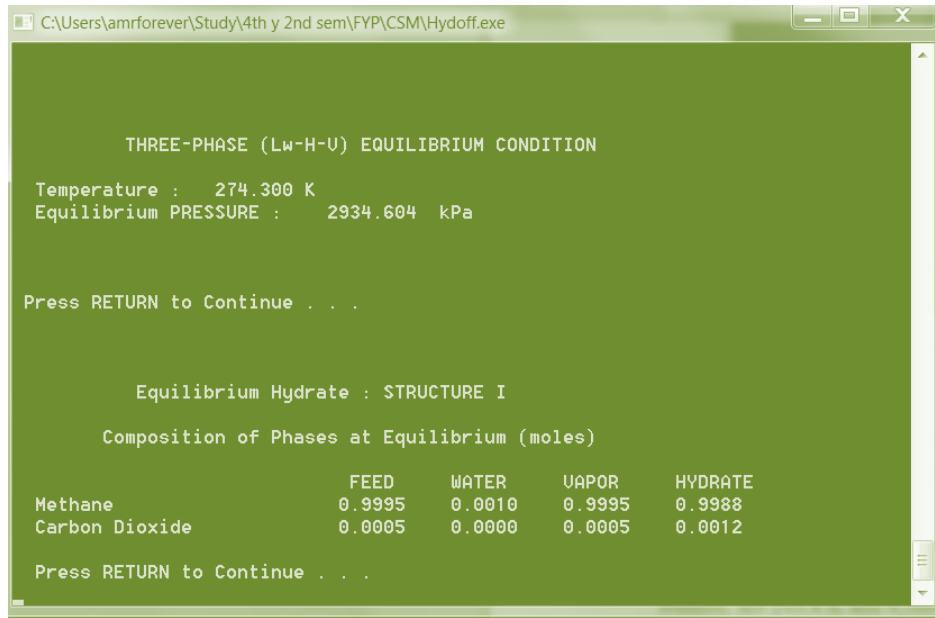


Figure 19: Equilibrium Pressure

Then the software shows some options that offer further analysis of the restored gas mixture. The option of interest for the sake of this simulation is “Specified T and P Flash”. Then the temperature is set to be 274.3 K and the pressure is set to be 4,500 kPa as shown in Figure 20.

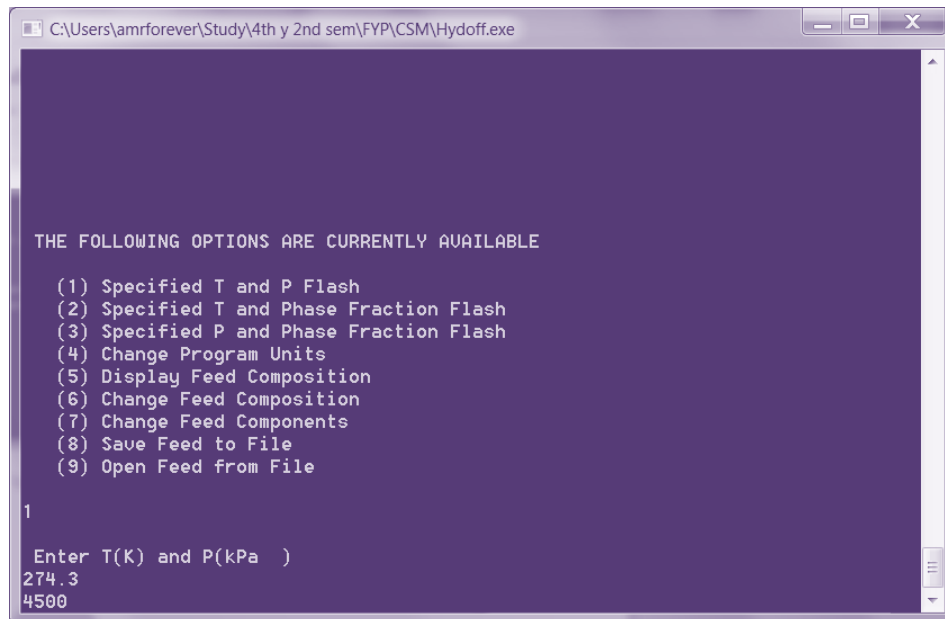
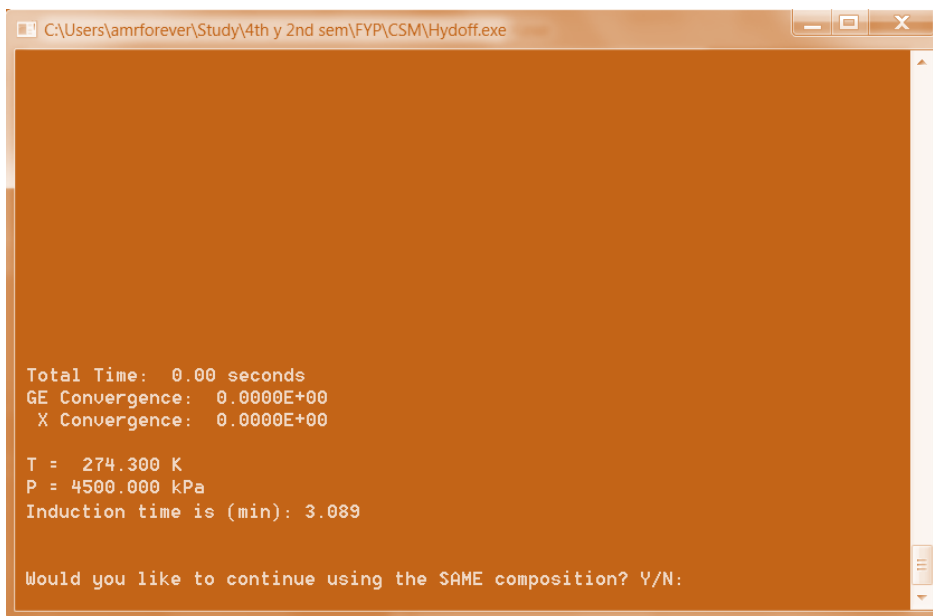


Figure 20: Specified T and P Flash

Once pressed Enter, the software shows the result of this simulation; as shown in Figure 21. Hydrates are formed in 3.089 minutes which is called the induction time.



```
C:\Users\amrforever\Study\4th y 2nd sem\FYP\CSM\Hydoff.exe

Total Time: 0.00 seconds
GE Convergence: 0.0000E+00
X Convergence: 0.0000E+00

T = 274.300 K
P = 4500.000 kPa
Induction time is (min): 3.089

Would you like to continue using the SAME composition? Y/N:
```

Figure 21: Induction time for the restored gas composition.

#### 4.3.2 Determining the best Degree of Deacetylation of Chitosan.

The objective of this step is to determine whether different DDs of Chitosan have different effects on hydrate formation inhibition or not. And, if they do, to determine the best DD to be used in determining the optimum concentration.

In order to study the effect of DD of Chitosan efficiently, equal weight percentages of different DDs are used. Any weight percentage can be used. For this simulation, the weight percentage to be used is 0.5 wt% of the water. In the lab experiment, this solution is prepared by adding 0.5 g of Chitosan of the desired DD to 100 mL of 5% acetic solution and then stirring this mixture for one hour. [10] Then 25 cc of this solution is injected into the PVT Cell of the Hydreval.

To simulate, the previous procedure is followed after adding one more component to the system which is Chitosan. This step starts from figure 4.3 onwards. The DD is simulated at 60%, 70%, 80%, 85% and 90%. The results are summarized and listed in Table 3.

Table 3: Simulation of different DD of Chitosan (0.5 wt%).

Simulation No.	DD (%)	Induction Time (min)
1	No Chitosan Only distilled water	3.089
2	60 %	54.341
3	70 %	81.102
4	80 %	115.869
5	85 %	128.248
6	90 %	117.637

This table can also be represented by the graph in Figure 22. It is interpreted from Table 3: Simulation of different DD of Chitosan (0.5 wt%). and the graph in Figure 22 that different DDs of Chitosan inhibit hydrate formation with different efficiencies which is reflected by the different induction times. It is noticed that the maximum induction time is obtained by using Chitosan with deacetylation degree of 85% after which the induction time starts to decrease. The next step is to determine the optimum concentration in terms of wt%.

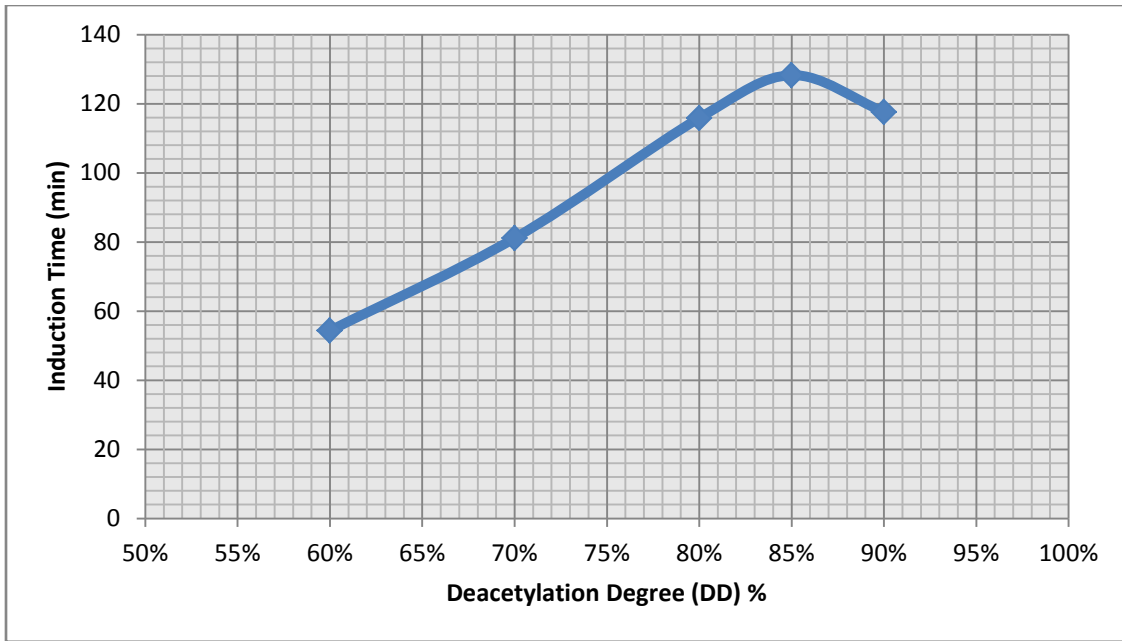


Figure 22: Induction time vs DD (0.5wt%)

#### 4.3.3 Determining the optimum Chitosan concentration of 85% DD.

Since the best deacetylation degree is determined to be 85% DD from the previous simulations. Now, the deacetylation degree is to be stabilized at 85% with changing the concentration. A concentration range from 0.2 wt% to 1.0 wt% is to be simulated. Same simulation procedure as the previous steps are followed after considering a constant deacetylation degree of 85% and different concentrations of 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt%, 0.9 wt% and 1.0 wt%. The results are listed in Table 4 and represented by the graph in Figure 23.

From the table and graph, it is interpreted that as the concentration of DD increases, the induction time increases and, hence, the efficiency of Chitosan as a kinetic hydrate inhibitor increases. However, for concentrations after 0.7 wt% the induction time shows slight increase that can be neglected. For that reason, the optimal concentration is chosen to be 0.7 wt%.

Table 4: Simulation of different concentrations of Chitosan with a DD of 85%.

Simulation No.	wt%	Induction Time (min)
7	0.2	72.890
8	0.3	91.602
9	0.4	109.726
10	0.5	128.248
11	0.6	135.262
12	0.7	141.231
13	0.8	145.048
14	0.9	147.605
15	1.0	146.792

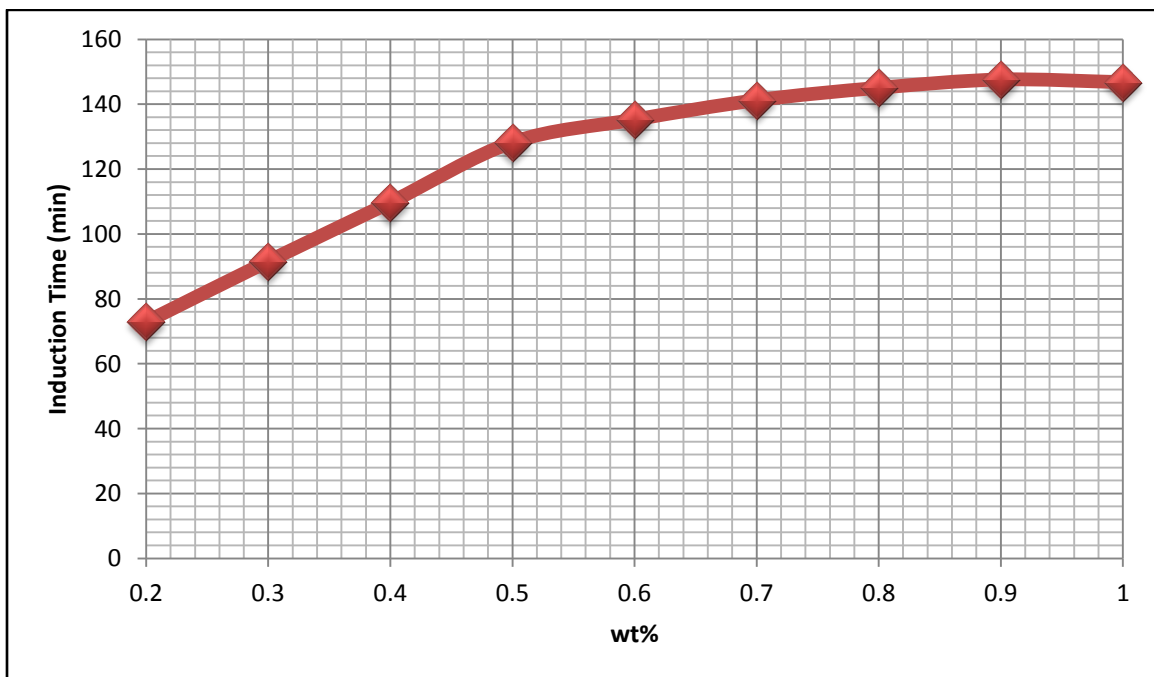


Figure 23: Induction time (min) vs wt% (85% DD)

Previous results from this simulation show that the optimal characteristics of Chitosan that is to be used as a methane hydrate green inhibitor is the Chitosan that has 85% deacetylation degree and weight percentage of 0.7. A solution of this Chitosan delays the nucleation of methane hydrate and keeps it from reaching the critical size to initiate the hydrate growth for about 141.231 minutes (2 hours and 21 minutes). A hydrate inhibitor is classified as weak if the induction time is less than one hour. [15] But for 85 % DD Chitosan with a concentration of 0.7 wt%, the induction time is more than two hours. Therefore, 85% DD Chitosan with a concentration of 0.7 wt% is considered a good Methane Kinetic Hydrate Inhibitor.



## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

Preventing hydrate formation is a very important procedure in gas flow insurance and gas processing. Hydrates are ice-like substances that are able to grow under certain conditions and result in plugging the pipeline, block the gas flow, reduce the production, pipeline damage and pipe corrosion. Hydrate formation inhibitors are classified into 3 types: Thermodynamic Hydrate Inhibitors (THIs), Kinetic Hydrate Inhibitors (KHIs) and Anti-Agglomerates (AAs). The focus of this research is on a type of KHI which is Chitosan. Simulation was conducted using Hydoff Software to determine the effectiveness of different deacetylation degrees of Chitosan as well as the optimum concentration. The composition of the gas mixture to be used is studied. Using Hydoff Software, the phase equilibrium properties of this mixture is known. The equilibrium pressure at 274.3 K is determined to be 2,934.604 kPa. Different degrees of Deacetylation of Chitosan, ranging from 60% to 90%, were investigated. The best DD Chitosan was found to be 85%. Then this Chitosan was investigated in terms of concentration (weight percentage). The optimal Chitosan was found to be 0.7% of 85% DD that would lead to an induction time of 2 hours and 21 minutes which is considered a very good inhibitor of hydrate formation.

It is recommended to confirm these results practically by using high pressure vessel equipments that are used to study the equilibrium behaviors of hydrates such as micro Differential Scanning Calorimeter ( $\mu$ -DSC) or Hydreval. It is also recommended to study the effect of Chitosan in combination with other hydrate inhibitors that showed effective results based on experimental data such as Polyvilylpyrrolidone (PVP) or Polyethyle Oxide (PEO). The combination of Chitosan with these inhibitors might give better results of hydrate inhibition and longer induction time.

## REFERENCES

- [1] J. Carroll, Natural Gas Hydrates, 1st ed. Burlington: Elsevier, 2002.
- [2] W. Harris, 'HowStuffWorks "A Brief History of Methane Hydrate"', HowStuffWorks, 2014. [Online]. Available: <http://science.howstuffworks.com/environmental/green-tech/energy-production/frozen-fuel2.htm>. [Accessed: 20- Feb- 2014].
- [3] E. Sloan and J. Bloys, Hydrate engineering, 1st ed. Richardson, Tex.: Society of Petroleum Engineers, 2000.
- [4] H. Abdel-Aal, M. Aggour and M. Fahim, Petroleum and gas field processing, 1st ed. New York: Marcel Dekker, 2003.
- [5] S. Hagen, 'hydrate inhibitors alternatives to straight methanol injection', in Northern Area Western Conference, Alberta, 2010.
- [6] Hdc.ca, 'Gas Line Heater Training Kit - HDC Human Development Consultants Ltd. - HDC', 2014. [Online]. Available: [https://www.hdc.ca/purchase\\_description.asp?ID=37](https://www.hdc.ca/purchase_description.asp?ID=37). [Accessed: 04- Feb- 2014].
- [7] A. Kidnay and W. Parrish, Fundamentals of natural gas processing, 1st ed. Boca Raton: CRC Press, 2006.
- [8] N. Ain Sapain, 'Evaluation on Effectiveness of Ionic Liquids as Kinetic Hydrate Inhibitor Using Micro Differential Scanning Calorimeter', Undergraduate, Universiti Teknologi PETRONAS, 2013.
- [9] J. PAEZ and R. Blok, 'Problems in Hydrates: Mechanisms and Elimination Methods', SPE Production and Operations Symposium, 2001.
- [10] S. Sariffuddin, 'Effect of natural polymers as kinetic inhibitor using micro-differential scanning calorimeter.', undergraduate, Universiti Teknologi PETRONAS, 2013.

- [11] Y. Xu, M. Yang and X. Yang, 'Chitosan as green kinetic inhibitors for gas hydrate formation', *Journal of Natural Gas Chemistry*, vol 19, iss 4, pp. 431-435, 2010.
- [12] O. Fandiño and L. Ruffine, 'Methane hydrate nucleation and growth from the bulk phase: Further insights into their mechanisms', *Fuel*, vol 117, pp. 442-449, 2014.
- [13] B. Partoon, N. Wong, K. Sabil, K. Nasrifar and M. Ahmad, 'A study on thermodynamics effect of [EMIM]-Cl and [OH-C2MIM]-Cl on methane hydrate equilibrium line', *Fluid Phase Equilibria*, vol 337, pp. 26-31, 2013.
- [14] Q. Nasir, K. Sabil and K. Nasrifar, 'Measurement and Phase Behavior Modeling (Dew Point+Bubble Point) of Co<sub>2</sub> Rich Gas Mixture', *Journal of Applied Sciences*, vol 14, iss 10, pp. 1061-1066, 2014.
- [15] J. Lee and P. Englezos, 'Enhancement of the performance of gas hydrate kinetic inhibitors with polyethylene oxide', *Chemical Engineering Science*, vol 60, iss 19, pp. 5323-5330, 2005.